

I. THE STRUCTURE OF VINYL POLYMERS
II. ADDENDUM

BY
EDWARD HOLLISTER RIDDLE
B.S., Harvard University, 1937

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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I. THE STRUCTURE OF VINYL POLYMERS

A. THE EFFECT OF CATALYSTS ON THE STRUCTURE OF VINYL POLYMERS

INTRODUCTION

Marvel and his students¹⁻⁴ have determined the structures of several vinyl polymers prepared with benzoyl peroxide catalysts. This investigation was undertaken to determine if these polymers have the same structure when prepared with different catalysts.

EXPERIMENTAL

Polyvinyl acetate was prepared by ultraviolet activation, in the absence of peroxides and oxygen, and with cadmium chloride as catalyst. Hydrolysis of these polyvinyl acetates gave the corresponding polyvinyl alcohols, which were not oxidized by periodic acid, showing that these polymers have the same structure as that prepared with peroxide catalyst,² namely, a "head to tail" structure, $(-\text{CH}_2-\text{CHX}-\text{CH}_2-\text{CHX}-)$. Polymerization of vinyl acetate with boron fluoride as catalyst invariably gave black insoluble powders which were low in oxygen content, and had evidently cross-linked by loss of acetic acid under the influence of boron fluoride, probably by the same type of reaction that Meerwein⁵ has postulated for the action of acetic anhydride on ketones in the presence of boron fluoride.

Methyl α -bromoacrylate has been polymerized under the influence of ultraviolet radiation, in the absence of peroxides and oxygen, and with a boron fluoride catalyst. These polymers lost 85-95% of their bromine when treated with potassium iodide, indicating that they have the same "head to head" structure, $(-\text{CH}_2\text{CHX}-\text{CHXCH}_2-)$, as the polymer of methyl α -bromoacrylate prepared with peroxide catalyst.³

Polymers of vinyl bromide, prepared with ultraviolet activation in the absence of peroxides and with a boron fluoride catalyst, did not liberate iodine from potassium iodide, thus indicating that these polymers have the same "head to tail" structure as the peroxide-catalyzed polyvinyl bromide.⁴ However, a considerable amount of bromine was lost as hydrogen bromide. Similarly, the reaction of polyvinyl bromide with zinc removed 95% of the bromine, which is far in excess of the 87% that should be removed according to statistical calculations.⁶ A sample of this

debrominated polymer decolorized dilute potassium permanganate solution, proving the presence of unsaturation in the product from treatment with zinc.

SUMMARY

Evidence has been presented to show that vinyl polymers formed by the action of catalysts such as peroxides and boron fluoride or by photochemical activation have the same arrangement of monomeric units in the polymer chain. The nature of the monomer unit determines whether the polymer has the "head to tail" or "head to head" structure.

Vinyl acetate loses acetic acid when polymerized by the action of boron fluoride complexes and the polymer is intractable.

Polyvinyl bromide loses hydrogen bromide as well as bromine when heated with zinc and hence this reaction is not useful for determining structure in this case.

B. THE POLYMER OF METHYL ISOPROPENYL KETONE

EXPERIMENTAL

Methyl isopropenyl ketone has been prepared from methyl ethyl ketone and formaldehyde,⁷ and the yields and molecular weights⁸ have been determined for polymers of this ketone prepared at 25° and 60° with peroxide catalyst and without catalyst and at 25° under the influence of ultraviolet light. Satisfactory polymers were obtained only by photochemical activation and by long standing of the monomer with benzoyl peroxide catalyst at 25°. Higher temperatures invariably gave yellow polymers, and a boron fluoride catalyst gave black insoluble products, comparable to the polymers from vinyl acetate with the same catalyst.

Pyrolysis of the polymer of methyl isopropenyl ketone at 270° in inert atmosphere for 5 hours removed 63% of the oxygen as water, through condensation of neighboring methyl ketone groups. Since a "head to head" polymer can lose a maximum of only 50% of its oxygen in this way, the polymer of methyl isopropenyl ketone must have the "head to tail" structure. A similar condensation was carried out by refluxing the polymer with sodium ethoxide, but only about 35% of the groups reacted. Hydrogenation of the polymer with Raney nickel for 17 hours at 200° gave a product whose analysis showed that most of the carbonyl groups were reduced, and many of the resulting alcohol groups were dehydrated.

SUMMARY

The preparation of methyl isopropenyl ketone and its polymerization under various conditions have been investigated. Pyrolysis of the polymer showed that it has the same "head to tail" structure as has been found for the polymer of methyl vinyl ketone.^{1a} The polymer has been made to undergo aldol condensation, and hydrogenation of the carbonyl groups, with subsequent dehydration, was accomplished.

II. ADDENDUM: THE CONDENSATION OF ACETALDEHYDE AND VINYL ACETATE

Bodendorf⁹ has suggested a mechanism for aldol condensation involving addition of the double bond of the enol form to the carbonyl group double bond of another molecule, forming a four-membered hemiacetal ring, which then rearranges to aldol. This is similar to the reaction of Prins¹⁰ in which formaldehyde was added to styrene. In an attempt to test this mechanism, Harmon¹¹ condensed vinyl acetate (ester of acetaldehyde enol) with acetaldehyde using sodium as a catalyst. The product has been shown to be a cyclic acetal formed from two molecules of acetaldehyde and one of vinyl acetate.

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VITA

The author was born in Wellesley, Mass., February 13, 1916. He attended the Shady Hill School, Cambridge, Mass.; Derby Academy, Hingham, Mass.; Thacher School, Ojai Valley, California; and was graduated from Phillips Exeter Academy, Exeter, N. H., in the spring of 1933. In the fall of that year he entered Harvard University, and received the degree of Bachelor of Science in the spring of 1937. In the following fall he entered the Graduate School of the University of Illinois, serving as assistant in chemistry from September, 1937 to August, 1939, and holding the Monsanto Fellowship from September, 1939 until June, 1941.

